LOW TEMPERATURE LITHIUM BATTERIES

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What Scientific Laws Govern Batteries' Cold Temperature Performance?

- Thermodynamic temperature term in Nernst Equation.
- Electrochemical kinetics dependence on temperature.
- Presence of solid electrolyte interface at the anode and possibly the cathode. SEI ionic conductivity shows a log response with temperature.
- Electrolyte ionic conductivity dependency on temperature.
- Solid state diffusion into a host electrode structure.

Lithium Inorganic Primary Batteries

SAFT is the largest supplier of lithium primary batteries for the US space and defense market

- **Thionyl Chloride – generally can operate at –40°C to –50°C in conventionally designed cells. For extreme operation –80°C has been achieved with reduced salt concentration. Ultimately the freezing point of $SOCl_2$ (-100°C) is the limiting factor.**
- **Sulfur Dioxide – generally can operate at –40 to –50°C. The same limiting factors apply – freezing point of acetonitrile/SO_2 solvent (-46°C/-73°C).**

SAFT Low Temperature Efforts

- **SAFT started low temperature lithium-ion cell development in mid 1990's**
  - Under automotive (PNGV) programs with DOE and USABC
  - Under TRP program with US Air Force and US Army
  - Ongoing Very High Power development effort with US Air Force
- **For most applications SAFT targets development of low temperature capabilities with limited or no impact on calendar and cycle life**

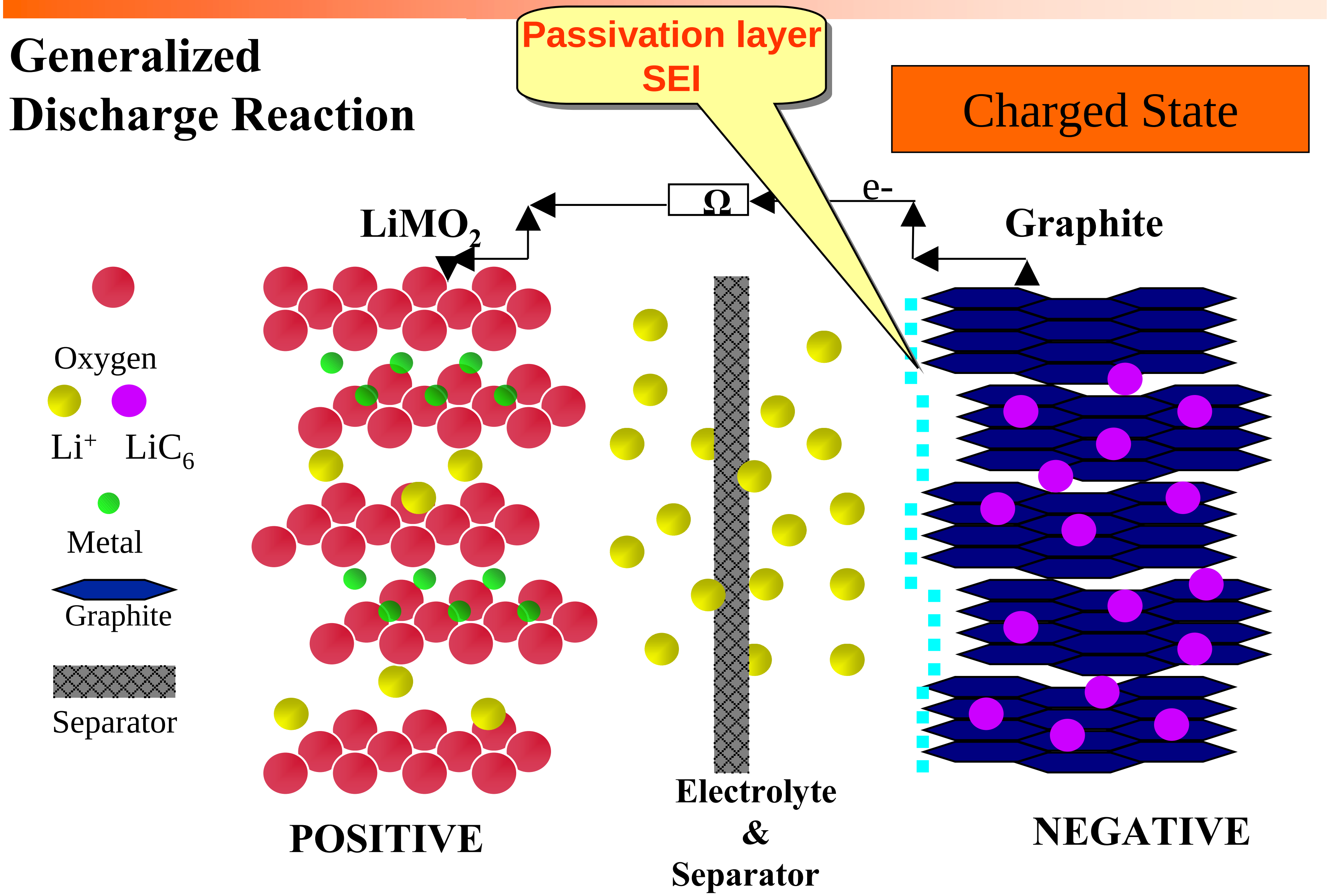
Steps Involved in Charge/Discharge

For Lithium-ion Electrochemistry

- **In liquid electrolyte electroactive species (ions) are transported between electrodes by migration and/or diffusion.**
- **When they reach the surface SEI, these species change phases (heterogeneous reactions).**
- **The ions undergo solid state ionic diffusion through the SEI to reach active electrode site.**
- **At the active electrode site an electron transfer step (Faradaic reaction) takes place.**
- **Finally lithium has to diffuse into the host lattice (metal oxide for discharge and carbon for charge).**

All of these steps are influenced by temperature. They induce consequent polarization terms that lower the operating voltage and limit material utilization at low temperature. Net effect is reduced energy and power delivered from batteries.

Generalized Discharge Reaction



Designing for Low Temperature Performance

- **Low temperature performance can be influenced by several different approaches:**
  - **Procure low temperature electrolytes**
    - Small percentage of solvent with high dielectric constant
    - Large percentage of solvents with low viscosity, low freezing point and good ionic conductivity
    - Lithium salt optimization.
  - **Select suitable active materials**
    - Carbons and positive active materials with fast kinetics and good Li diffusion coefficient at low temperature
  - **Design electrode morphology**
    - Optimize porosity, pore size and wetability of electrodes

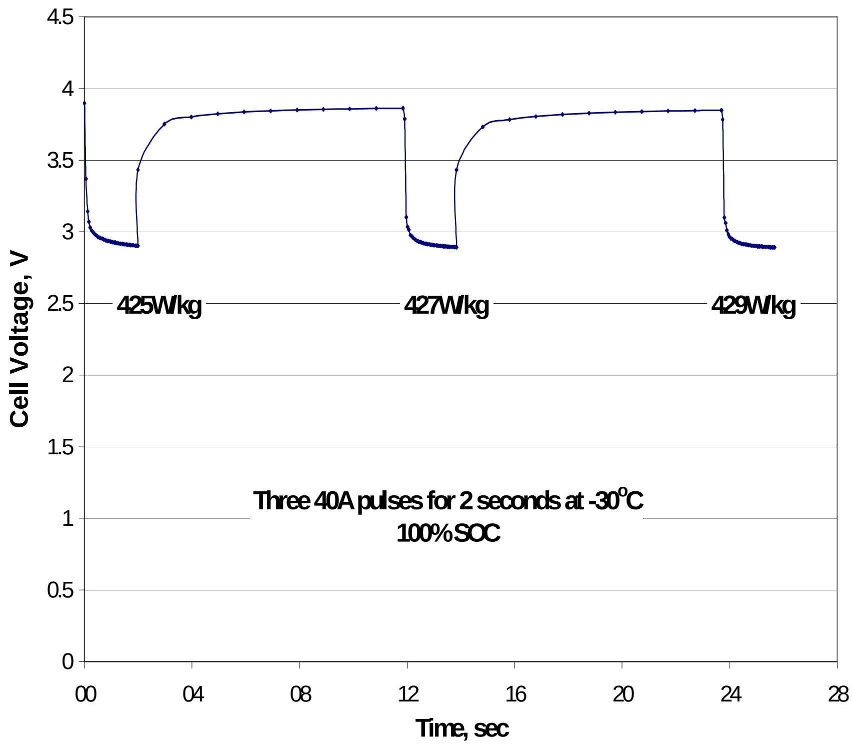
Low Temperature Electrolyte

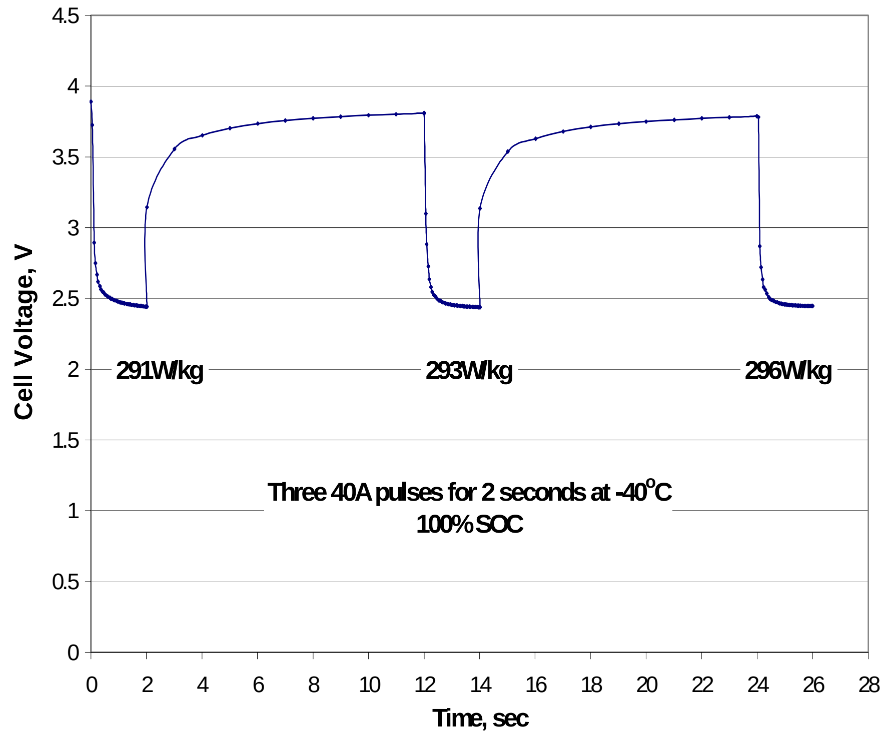
- **Low temperature electrolytes in general should contain:**
  - Low quantity of EC
  - Large quantity of low viscosity, low freezing point and high conductivity solvents like EMC, DMC, EA, etc..
- **The drawback is:**
  - Reduced life and stability at elevated temperature

Solvent	Dielectric Constant	Conductivity, mS/cm		Viscosity, $kg.m^{-1}s^{-1}$		T_{FREEZE}, Deg C
		25°C	-20°C	25°C	-20°C	
Ethylene Carbonate, EC	89.6	5.2	-	1.9	-	39.4°C
Propylene Carbonate, PC	64.4	6.9	1.1	2.33	7.41	-49°C
DiEthyl Carbonate, DEC	2.82	2.9	1.4	0.75	-	-43°C
DiMethyl Carbonate, DMC	3.1	6.5	1.4	0.59	-	3°C
Ethyl Methyl Carbonate, EMC	2.4	4.3	2.2	0.7	1.29	-55°C
Ethyl Acetate, EA	6	11	6.6	0.51	0.85	-83°C

SAFT Automotive Li-ion Technology

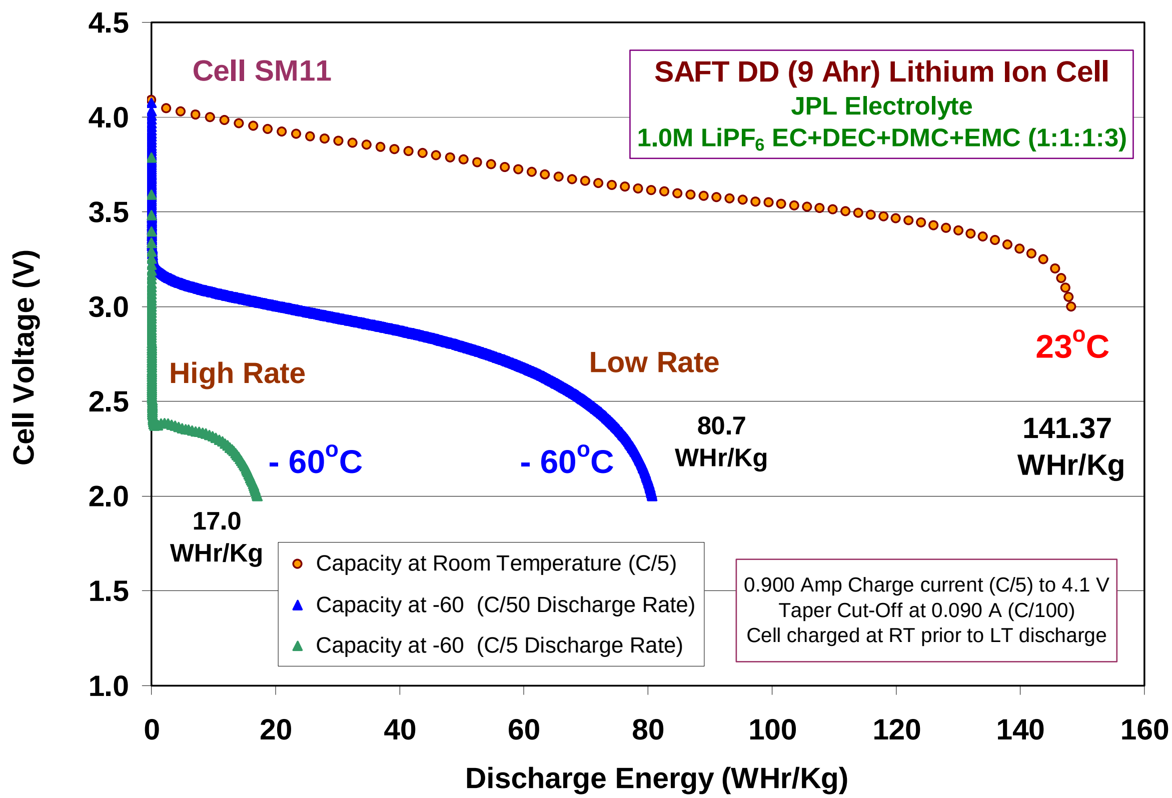
- Low temperature capability needed for Cold Cranking
- Battery for Hybrid Electric Vehicle developed based on 36 lithium-ion cells containing SAFT automotive low temperature electrolyte





Low Temperature Electrolyte for Space

- SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications
- Discharge Rate Capability at - 60°C with JPL Electrolyte



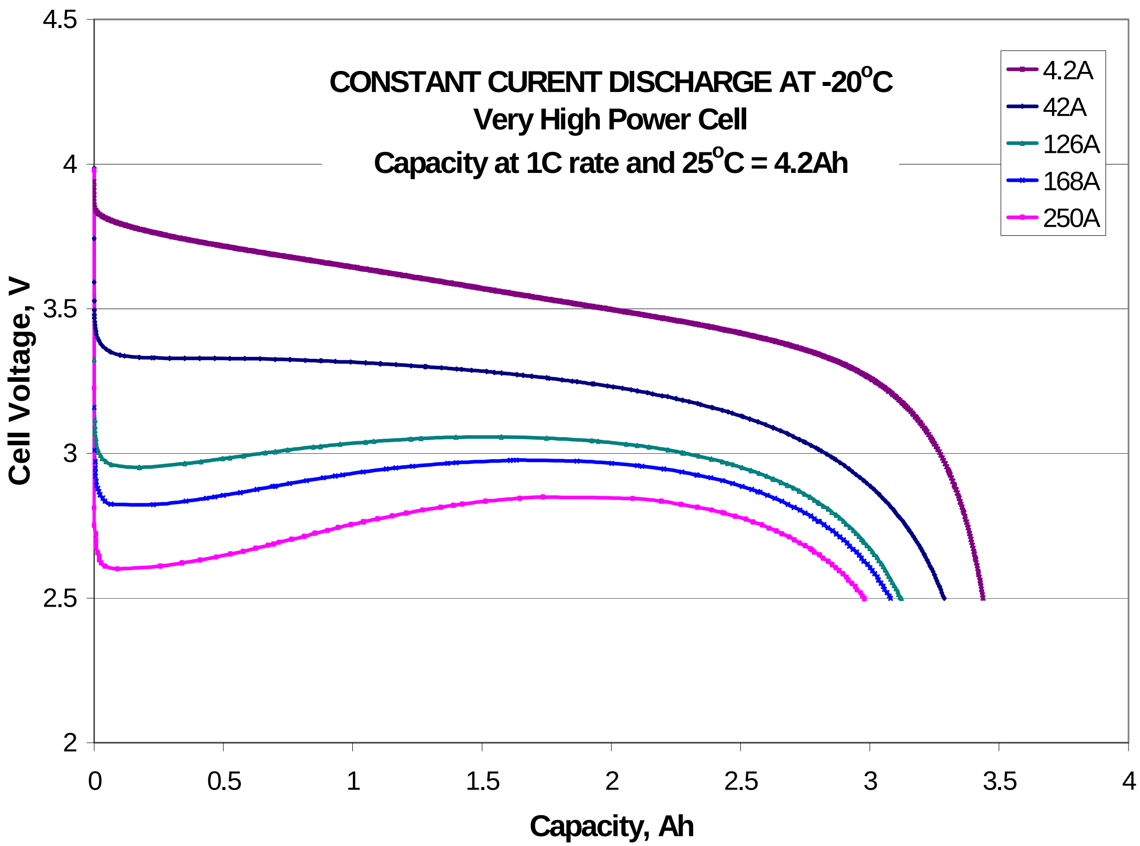
Courtesy of JPL (Graph provided by Marshal Smart)

Low Temperature Performance Improvement Through Electrode Optimization

- **Active materials**
  - Use of carbon materials specifically screened for low temperature charge acceptance and electrical properties
  - Use of modified positive active materials
- **Electrode morphology**
  - Optimized porosity and pore size distribution
  - Optimized binders and conductive diluents for best wetability and maximized electrochemically active area

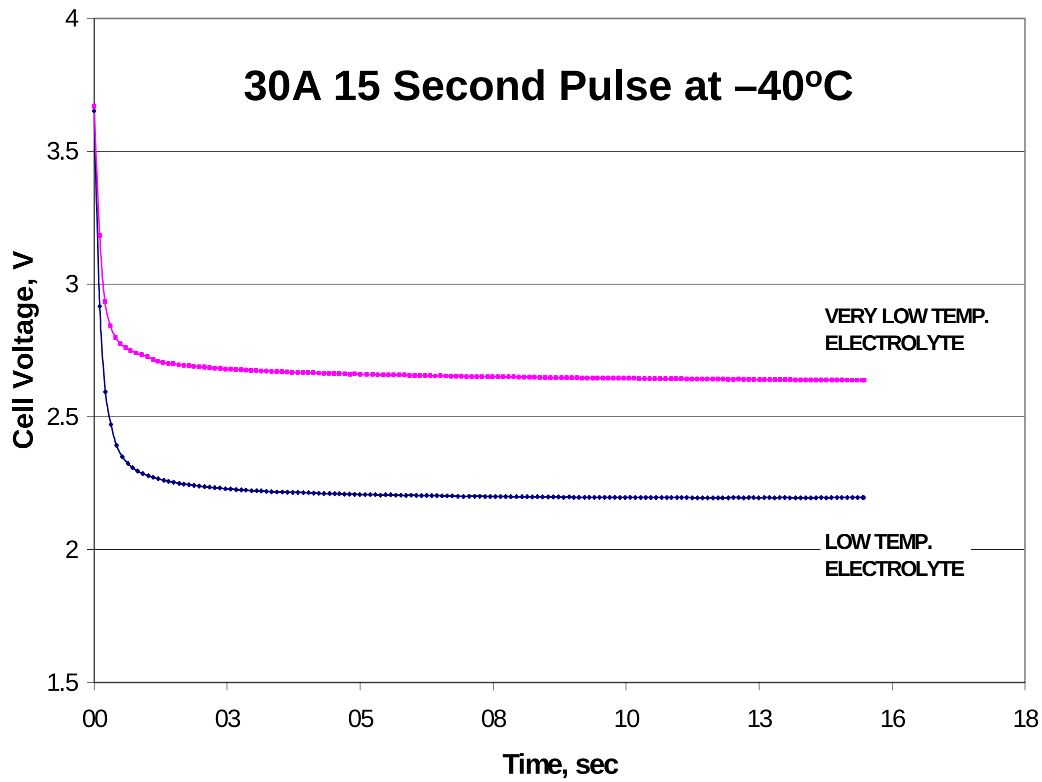
Very High Power Lithium-ion Cell

- Developed under contract with US Air Force



Very High Power Lithium-ion Cell

- Low temperature electrolyte is optimized for both low and high temperature exposure
- Very low temperature electrolyte is maximized for low temperature performance but it is not very good for elevated temperature



Challenges in Front of Low Temperature Batteries

- **Charge acceptance at low temperature is affected by two main factors:**
  - Severely reduced ionic conductivity in the electrolyte. Polarization across the electrode thickness becomes very important.
  - Solid state diffusion (lithium diffusion in carbon materials) slows down at low temperature. This could become a rate limiting step.

  Both of these limitations force some lithium to be plated as metallic lithium on the surface of the carbon electrode.

- **Extreme low temperature operation**
  - Most low temperature solvents freeze at around -40 to -80^{o}C. This limits the practical useful low temperature operation of Li-ion.

What is Needed to Overcome These Challenges?

- **Development of novel intercalation electrodes -** faster kinetics, better solid state diffusion properties, thermodynamic and electrochemical stability. One example would be the use of lithium titanates but their use would result in lower energy density.

- **Research on novel solvents -** much broader liquid temperature range, improved ionic conductivity especially at low temperature, better electrochemical stability.

- **Novel salts –** most commonly used Li salts, $LiPF_6$, start decomposing at temperatures around 65^{o}C.

Organizations Working on Low Temperature Batteries

- Jet Propulsion Laboratory
- US National Laboratories under ATD DOE funding
- US Army – The group of Edward Plichta in CECOM, Fort Monmouth NJ, and the group of Richard Jow in ARL, Adelphi MD
- Other US battery companies – work is normally focused on requirements of existing funded project and usually does not extend to extreme environments

Future of
Low Temperature Batteries

- Current state-of-the art lithium-ion batteries deliver the best low temperature performance among rechargeable batteries.

- Even the performance of the best low temperature battery today is not meeting the requirements of the new space missions. More fundamental work on the electrodes and solvents is needed to extend the capability of the technology.